

Breakdown of the Rosenfeld Excess Entropy Scaling Relations for the Core-Softened Systems: Thermodynamic Path Dependence

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We analyze the applicability of the Rosenfeld entropy scaling relations to the systems with the core-softened potentials demonstrating the water-like anomalies. It is shown that the validity of the of Rosenfeld scaling relation for the diffusion coefficient depends on the thermodynamic path which is used for the calculations of the kinetic coefficients and the excess entropy. In particular, it is valid along isochors, but it breaks down along isotherms.

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In 1977 Rosenfeld proposed the relations connecting transport properties of a liquid with the excess entropy [1]. In order to write down these relations one should use the reduced forms of the transport coefficients:

$$D^* = D \frac{\rho^{1/3}}{(k_B T/m)^{1/2}} \quad (1)$$

$$\eta^* = \eta \frac{\rho^{-2/3}}{(mk_B T)^{1/2}} \quad (2)$$

where D and η are the diffusion coefficient and the viscosity. According to the Rosenfeld suggestion, the reduced transport coefficients can be expressed in the form

$$X = a_X \cdot e^{b_X S_{ex}}, \quad (3)$$

where $S_{ex} = (S - S_{id})/(Nk_B)$ is excess entropy of the liquid, X is the transport coefficient, and a_X and b_X are the constants which depend on the studying property [2]. Interestingly, the coefficients a and b show an extremely weak dependence on the material and can be considered as universal.

In his original works Rosenfeld considered hard spheres, soft spheres, Lennard-Jones system and one-component plasma [1, 2]. After that the excess entropy scaling was applied to many different systems including core-softened liquids [3–7], liquid metals [8, 9], binary mixtures [10, 11], ionic liquids [12, 13], network-forming liquids [3, 12], water [14], chain fluids [15] and bounded potentials [7, 16, 17].

Nevertheless, controversies still remain. For example, up to the moment it is not clear whether the Rosenfeld scaling relations are applicable to the core softened systems. Some publications state that the scaling relations are valid for such systems [5, 6], while in our recent work it was shown that the scaling relations may break down for the core softened systems [7]. This article presents a discussion of this contradiction. Basing on the molecular dynamics simulations of the two core-softened systems we show that the validity of the Rosenfeld scaling relations depends on the thermodynamic path which is used

for the calculations of the kinetic coefficients and the excess entropy. In particular, the exponential functional form of the relation between the excess entropy and the reduced diffusion coefficient holds along isochors while along isotherms one observes its breakdown.

Two systems are studied in the present work. The first one is the core-softened system introduced by de Oliveira et al [18]. This system is described by the spherically symmetric potential represented by a sum of a Lennard-Jones contribution and a Gaussian-core interaction (LJG):

$$U(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + a\varepsilon \cdot \exp \left[-\frac{1}{c^2} \left(\frac{r - r_0}{\sigma_0} \right)^2 \right], \quad (4)$$

with $a = 5.0$, $r_0/\sigma = 0.7$ and $c = 1.0$. This model can qualitatively reproduce water's density, diffusivity, and structural anomalies. The diffusivity of this system was studied, for example, in the papers [6, 18]. In the papers [5, 6] the validity of the Rosenfeld scaling relation for this system was checked. In this paper we discuss these results and compare them with our calculations.

The second system studied in this work is a repulsive shoulder system (RSS) introduced in our previous work [19]. This system has a potential

$$U(r) = \left(\frac{\sigma}{r} \right)^{14} + \frac{1}{2}\varepsilon \cdot [1 - \tanh(k_0\{r - \sigma_1\})], \quad (5)$$

where σ is the "hard"-core diameter, $\sigma_1 = 1.35$ is the soft-core diameter, and $k_0 = 10.0$. In Ref. [20] it was shown that this system demonstrates anomalous thermodynamic behavior. In our previous publication [7] the Rosenfeld relation for this system was studied. It was shown that the scaling relation for the diffusion coefficient breaks down for this system in the anomalous diffusion region.

In this paper we use the dimensionless quantities: $\tilde{\mathbf{r}} = \mathbf{r}/\sigma$, $\tilde{P} = P\sigma^3/\varepsilon$, $\tilde{V} = V/N\sigma^3 = 1/\tilde{\rho}$, $\tilde{T} = k_B T/\varepsilon$. Since we use only these reduced units we omit the tilde marks.

For the investigation of the LJG potential we simulate a system of 1000 particles in a cubic box for the densities ranging from $\rho = 0.01$ till $\rho = 0.35$ with the

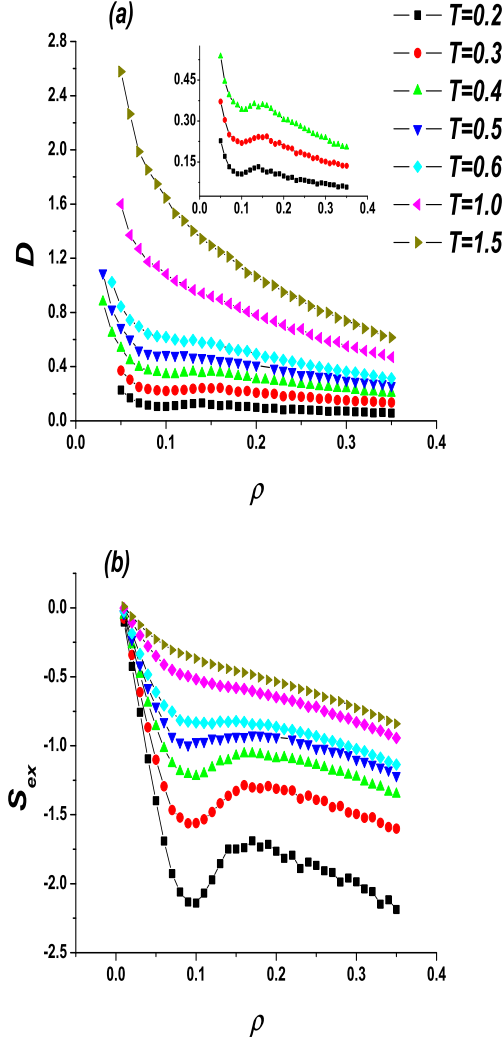


FIG. 1: (a) The diffusion coefficient of the LJG system along some isotherms. (b) The excess entropy of the LJG system for a set of isotherms. (Color online)

step $\delta\rho = 0.01$. The time step used is $dt = 0.001$. The equilibration period consists of $1 \cdot 10^6$ time steps and the production period - $2.5 \cdot 10^6$ time steps. During the equilibration the temperature is kept constant by velocity rescaling while during the production cycle NVE -MD is used. The equations of motion are integrated by velocity-Verlet algorithm. The following isotherms are simulated: $T = 0.2; 0.3; 0.4; 0.5; 0.6; 1.0$ and 1.5 .

The simulation setup of the RSS was described in Ref. [7].

The excess entropy in both cases was computed via thermodynamic integration method. For doing this we calculate excess free energy by integrating the equation of state along an isotherm: $\frac{F_{ex}}{Nk_B T} = \frac{F - F_{id}}{Nk_B T} = \frac{1}{k_B T} \int_0^\rho \frac{P(\rho') - \rho' k_B T}{\rho'^2} d\rho'$. The excess entropy is computed via $S_{ex} = \frac{U - F_{ex}}{Nk_B T}$.

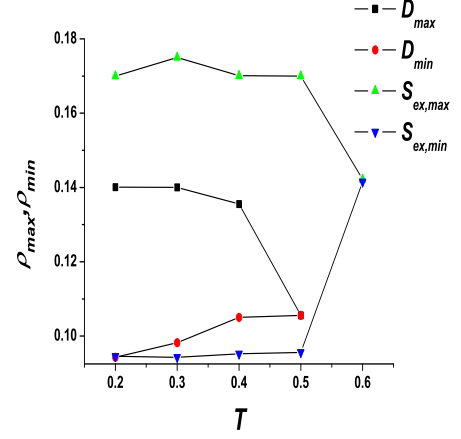


FIG. 2: The densities of maximum and minimum of the diffusivity and the excess entropy for the several isotherms.

Fig. 1(a) presents the diffusion coefficient of the LJG system along a set of isotherms. One can see that at low temperatures the diffusion coefficient shows nonmonotonic behavior which is known as the diffusion anomaly. Fig. 1(b) demonstrates the excess entropy for the same set of isotherms. From these figures it follows that the diffusion coefficient and the excess entropy along an isotherm have similar qualitative behavior. However, the location of the extremum points of diffusivity and excess entropy is different (Fig. 2). It means that there are some regions where one function increases while another one decreases and vice versa. Clearly, this kind of behavior can not be consistent with the Rosenfeld scaling formula. From this one can conclude that the Rosenfeld scaling relation is not applicable to the diffusivity along an isotherm for the LJG model.

Fig. 3 presents the logarithm of reduced diffusion coefficient vs excess entropy along a set of isotherms. One can see that at low temperatures the curves demonstrate a selfcrossing loop like the one observed for the RSS model in Ref. [7]. This loop becomes less pronounced with increasing the temperature and at $T = 0.5$ the self crossing disappears. At high temperatures the curve comes to the straight line limit which corresponds to the small influence of the soft core at such temperatures.

It can be seen from Figs. 1(a) and (b), that both the diffusivity and the excess entropy along isochors are monotonous (this corresponds to the vertical lines through the data points). It allows to expect that the exponential relation between the diffusion coefficient and the excess entropy holds along isochors. Fig. 4 shows the $\ln(D^*)$ vs S_{ex} along a set of isochors. From this figure one can see that all curves with good accuracy correspond to the Rosenfeld scaling relation. This result is in agreement with Refs. [5, 6].

In order to show that the dependence of the Rosenfeld scaling relations on the thermodynamic path is a general

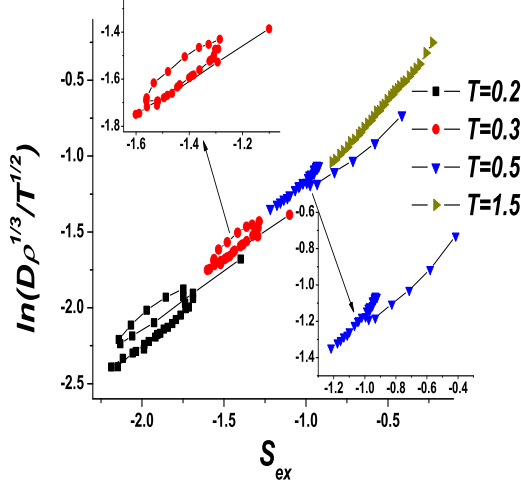


FIG. 3: The logarithm of the reduced diffusion coefficient for the LJM model along the several isotherms. The insets correspond to the temperatures $T = 0.3$ (upper panel) and $T = 0.5$ (lower panel) in the larger scale. (Color online)

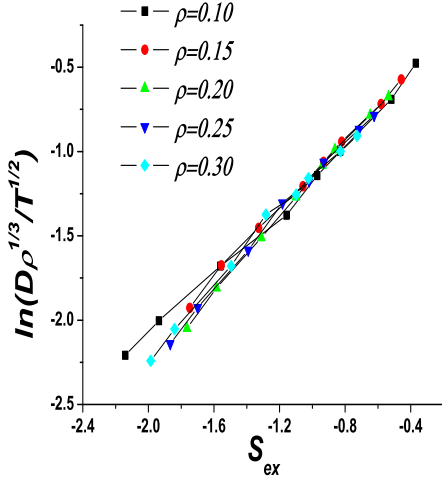


FIG. 4: The logarithm of the reduced diffusion coefficient for the LJM model along the several isochors. (Color online)

property of the core-softened systems we study another core softened potential introduced above - the repulsive shoulder system (RSS). In our previous publications we showed that this system demonstrates anomalous diffusion behavior at low temperatures [20] and that the Rosenfeld scaling relation along isotherms is not applicable [7]: the curves demonstrate the self crossing loops like in the case of the LJM system. Fig. 5 shows the logarithm of the reduced diffusion coefficient along a set of isochors for the RSS. As it can be seen from this figure, the dependence of D^* on S_{ex} is linear. However, the slope of the line shows an isochor dependence. Fig. 5 shows that

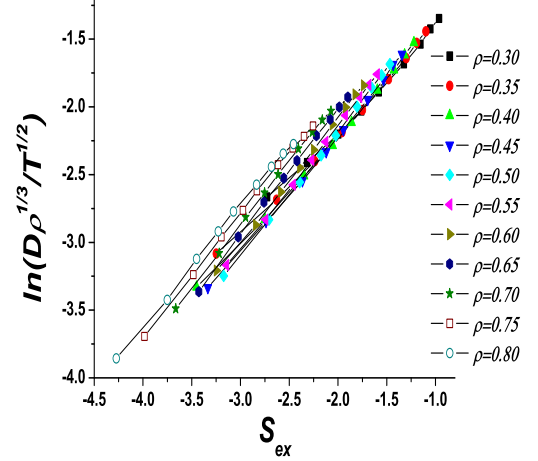


FIG. 5: Reduced diffusion logarithm for RSS along a set of isochors.

the slope remains approximately constant for low densities ($\rho = 0.3 - 0.55$) while on increasing the density the slope also increases.

The diffusion coefficient along isotherms as a function of the density and the reduced diffusion coefficient as a function of excess entropy are shown in Figs. 6(a) and (b). As it can be seen from Fig. 6(a), the density $\rho = 0.55$ corresponds to the density maximum at $T = 0.2$. In Ref. [19] it was shown that this system is effectively quasibinary. The reason for the complex behavior of this system is related to the competition between two length scales σ and σ_1 . This allows to suggest that the density $\rho = 0.55$ belongs to the boundary between two different regimes. It seems that the densities from $\rho = 0.6$ till $\rho = 0.8$ belong to a cross section region between low- and high-density regimes which leads to the shift of all curves with respect to each other. One can expect that at higher densities the logarithm of D^* comes to a straight line again but the slope of this line should be different from that at low densities.

In conclusion, in the present article we carry out a study of applicability of the Rosenfeld excess entropy scaling relation for the diffusion coefficient in the case of the systems with the core-softened potentials. We find that the validity of the of Rosenfeld scaling relation depends on the thermodynamic path. In particular, it is valid along isochors (although the scaling parameters show the isochor dependence), but it breaks down along isotherms. Interestingly, both the excess entropy and the diffusivity are monotonous along isochors while along isotherms they show the anomalous increase at low temperatures. It is this inconsistency in the location of the minimum and maximum points of the diffusion coefficient and the excess entropy along the isotherms which leads to the breakdown of Rosenfeld scaling relation for

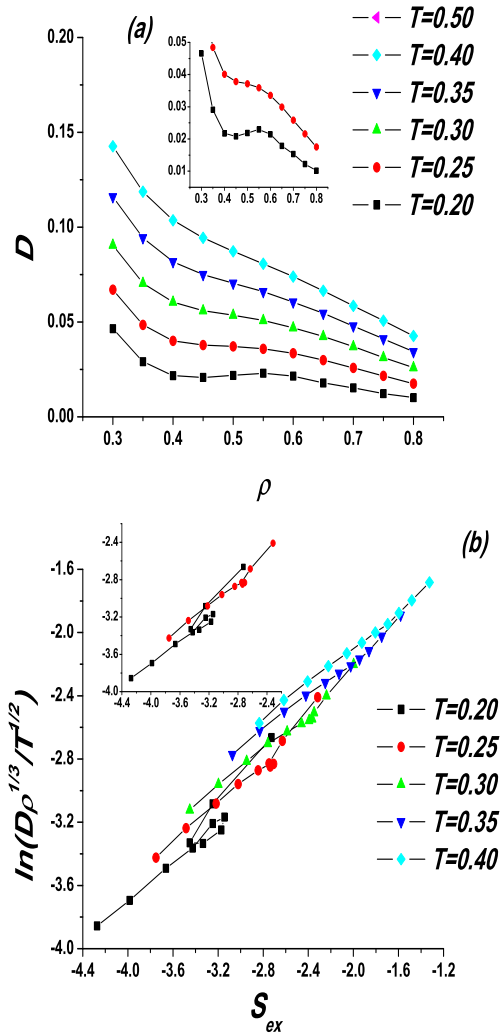


FIG. 6: (a) The diffusion coefficient for the RSS system along several isotherms. The inset enlarges the isotherms $T = 0.2$ (squares) and $T = 0.25$ (circles). (b) The logarithm of the reduced diffusion coefficient as a function of S_{ex} along a set of isotherms for RSS. (Color online).

these systems. This allows to suggest that the scaling relation is valid for the core-softened systems along any thermodynamic path if both S_{ex} and D^* are monotonous along it. However, this suggestion requires further investigation.

Another class of systems which attract a lot of attention with respect to the Rosenfeld scaling relation is bounded potential systems [7, 16, 17]. It is important to note that the conclusion of this paper is not applicable to these systems. For example, in Refs. [16, 17] scaling relation for the Gauss Core Model ([21]) along isochors was studied. According to these publications, the curves deviate from exponential dependence. This

allows to suggest that the relation between the dynamic and thermodynamic properties for the bounded potential systems is different from the systems with the hard core.

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